

Semivolatile particulate organic material in southern Africa during SAFARI 2000

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[1] During August and September 2000, the University of Washington's (UW) Cloud and Aerosol Research Group (CARG) with its Convair-580 research aircraft participated in the Southern African Fire-Atmosphere Research Initiative (SAFARI) 2000 field study in southern Africa. Aboard this aircraft was a Particle Concentrator-Brigham Young University Organic Sampling System (PC-BOSS), which was used to determine semivolatile particulate material with a diffusion denuder sampler. Denuded quartz filters and sorbent beds in series were used to measure nonvolatile and semivolatile materials, respectively. Results obtained with the PC-BOSS are compared to those obtained with conventional quartz-quartz and Teflon-quartz filter pack samplers. Various 10–120 min integrated samples were collected during flights through the free troposphere, in the atmospheric boundary layer, and in plumes from savanna fires. Significant fine particulate semivolatile organic compounds (SVOC) were found in all samples. The SVOC was not collected by conventional filter pack samplers and therefore would not have been determined in previous studies that used only filter pack samplers. The SVOC averaged 24% of the fine particulate mass in emissions from the fires and 36% of the fine particulate mass in boundary layer samples heavily impacted by aged emissions from savanna fires. Concentrations of fine particulate material in the atmospheric mixed layer heavily impacted by aged savanna fire emissions averaged $130 \mu\text{g m}^{-3}$. This aerosol was 85% carbonaceous material. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry

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1. Introduction

[2] During August and September 2000, the University of Washington's (UW) Cloud and Aerosol Research Group (CARG) participated with its UW Convair-580 research aircraft in the Southern African Fire-Atmosphere Research Initiative (SAFARI) 2000 field study in southern Africa. The Convair-580 was based out of Pietersburg, South Africa, during the first part of the study and out of Walvis Bay, Namibia, during the latter part. Details of the Convair-580 flights are given elsewhere [Hobbs, 2001; Sinha *et al.*, 2003]. The main objectives of SAFARI 2000 were (1) to provide in situ validation data for remote sensing measurements from the NASA ER-2 aircraft and the EOS Terra

satellite, (2) to obtain measurements needed to evaluate the contributions of emissions from biogenic, biomass burning, and industrial sources to the subcontinental haze over southern Africa, and (3) to study the evolution of the regional haze as it is transported in a counterclockwise gyre over the subcontinent. In addition, during the last 2 weeks of this field project, the Convair-580 participated with the NASA ER-2 in a study of marine stratus clouds off the Namibia coast.

[3] As part of the instrumentation aboard the Convair-580, a Particle Concentrator-Brigham Young University Organic Sampling System (PC-BOSS) was used to determine semivolatile particulate material with a diffusion denuder sampler. In addition, samples were collected for the determination of carbonaceous material using conventional filter pack samplers. The results obtained in flights in the free troposphere, in the boundary layer over South

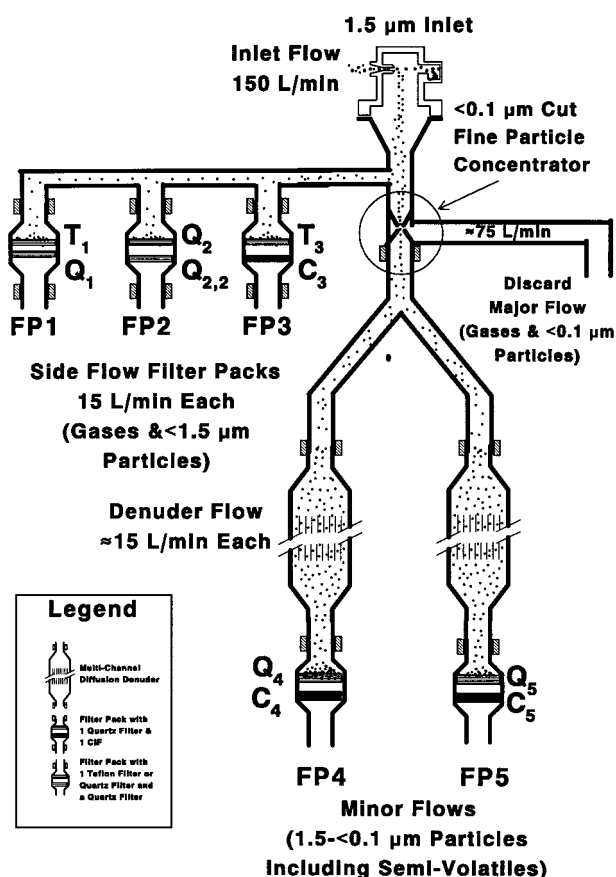


Figure 1. Schematic of the PC-BOSS (FP₃, FP₄, and FP₅) and conventional filter pack samplers (FP₁ and FP₂) used aboard the UW Convair-580 research aircraft during the SAFARI 2000 field study.

Africa, Zambia, and Botswana, and in smoke plumes from biomass fires are described in this paper.

2. Experimental

2.1. The PC-BOSS

[4] The PC-BOSS has been described elsewhere [Ding *et al.*, 2002; Lewtas *et al.*, 2001; Pang *et al.*, 2001]. A schematic of the PC-BOSS sampler that was used on the Convair-580 in SAFARI 2000 is given in Figure 1. The concentrations and composition of fine particles ($<1.5 \mu\text{m}$ aerodynamic diameter pass the inlet virtual impactor under the flow conditions used in this study) were determined from particles collected after they had passed through a particle concentrator (virtual impactor with a cut point $<0.1 \mu\text{m}$, resulting in concentrated particles in the $0.1\text{--}1.5 \mu\text{m}$ size range) and a BOSS charcoal denuder (Figure 1) to remove gas-phase sulfur dioxide, nitric acid and semivolatile organic compounds (SVOC) with a combined efficiency for the particle concentrator and denuder that exceeds 99% [Ding *et al.*, 2002; Lewtas *et al.*, 2001]. The denuder was followed by two parallel filter packs. Each of the parallel filter packs contained a 47 mm quartz filter (Gelman Sciences, Ann Arbor, MI, USA, Q₄ or Q₅ in Figure 1) followed by a 47 mm charcoal impregnated glass fiber filter

(CIG, Schleicher and Schuell, Dassel, Germany, C₄ or C₅ in Figure 1). Both filters were masked to give only a circular 19 mm sample collection area to improve the limit of quantification for carbonaceous material. This combination of filters was used to determine fine particulate carbonaceous material, sulfate, and nonvolatile nitrate on the quartz filter, and semivolatile nitrate and organic material lost from the particles on the quartz and trapped on the sorbent CIG. The parallel filter packs allowed the evaluation of data precision for the PC-BOSS during SAFARI 2000. In addition, there were three side-flow filter packs where particles were collected without passing through a particle concentrator or a denuder.

[5] The samples collected in filter packs 1 and 2 (Figure 1) were conventional filter packs similar to those that have been used in studies of fine particulate carbonaceous material [Kirchstetter *et al.*, 2001; Turpin *et al.*, 1994]. The sulfate material collected on the Teflon filter in filter pack 3 (T₃ in Figure 1) was used to evaluate the particle concentrator efficiency [Ding *et al.*, 2002; Lewtas *et al.*, 2001] for the collected samples.

2.2. Sampling

[6] Samples were collected aboard the Convair-580 during August and September 2000. A complete list of the instruments aboard the Convair-580, the flight strategies, and the various flights made in SAFARI 2000, have been described [Hobbs, 2001; Sinha *et al.*, 2003]. The flight numbers and details of the flights given below are identified by Hobbs [2003]. The portions of each flight where the twenty one PC-BOSS sample sets were collected, during flights based out of Pietersburg, South Africa, can be classified into eight categories (numbers in parenthesis are the UW flight numbers) [Sinha *et al.*, 2003]: in the free troposphere (UW 1821), from $\sim 60 \text{ m}$ to 2.6 km above the Indian Ocean (Inhaca Island, UW 1822), in the boundary layer over South Africa before 21 August (UW 1810, 1812, 1814, 1815, and 1819), boundary layer over South Africa after 22 August (UW 1820 and 1822), in boundary layer near the South Africa–Zambia border (UW 1823 and 1826), in boundary layer over Zambia (UW 1831), boundary layer over Botswana (UW 1829, 1832, and 1833), and in smoke plumes from savanna fires (UW 1816, 1819, 1826, 1831, and 1834).

2.3. Analytical Methods

2.3.1. Temperature Programmed Volatilization (TPV) Analysis

[7] TPV [Ellis and Novakov, 1982; Tang *et al.*, 1994] was used in the analysis of collected samples for total carbonaceous material. In this method, the various sample filters are heated from ambient temperature to a predetermined termination temperature at a predetermined rate. The rate of temperature increase and termination temperatures is dependent on the type of filter being analyzed. Quartz filters are heated at a rate of $28^\circ\text{C min}^{-1}$ to 800°C in an 80%/20% N₂/O₂ atmosphere. Charcoal impregnated filters are heated at a rate of $15^\circ\text{C min}^{-1}$ to 400°C in an N₂ atmosphere. Carbon in compounds desorbed from the filters during the heating process is catalytically converted to CO₂ and detected by nondispersive infrared absorption spectroscopy. Carbonaceous material retained by the Q₄ or Q₅ quartz

Table 1. Results of the Statistical Comparison of Replicate Data^a

Comparison	Linear Regression Analysis				Average	Bias ^b	σ^b	$\sigma\%^c$
	N	R ²	Slope	Intercept				
Ammonium Sulfate	14	0.97	0.96 ± 0.05	-0.5 ± 1.3	8.8	0.8	0.72	8.6
Ammonium Nitrate	15	0.96	0.87 ± 0.05	-0.4 ± 0.9	3.2	0.8	0.54	19
Total Nonvolatile Carbon	18	0.94	0.99 ± 0.06	0.5 ± 3.8	19.3	-0.3	2.5	13
SVOC	15	0.98	1.06 ± 0.04	-0.3 ± 2.9	16.0	-0.6	2.0	13

^aConcentrations are $\mu\text{g m}^{-3}$.^bSee (1).^cSee (2).

filters (Figure 1) is defined as “nonvolatile” in this paper and carbonaceous material which is lost from the particles during sampling and collected on the C₄ or C₅ charcoal filter (Figure 1) is defined as “semivolatile” in this paper. All carbonaceous material on those filters was analyzed by thermal desorption of the collected materials using TPV.

2.3.2. Evolved Gas Analysis (EGA) Analysis

[8] The EGA method described by Novakov [1981, 1982] was used to quantify total carbon content (TC) on the T₁ (to 450°C only), Q₁, Q₂ and Q_{2.2} filters (Figure 1). TPV and EGA are similar techniques. In EGA, a portion of the filter is heated at a constant rate (40°C min⁻¹ in this case) from 50° to 800°C in an oxygen atmosphere. The carbon-containing gases that evolve from the sample are converted to CO₂ over a manganese dioxide catalyst maintained at 800°C, which is subsequently measured with a nondispersive infrared analyzer (Beckman Model 870). A plot of the CO₂ concentration versus temperature is called a thermogram. The area under a thermogram is proportional to the TC content of the analyzed sample. The tandem filter method (FP1 and FP2 in Figure 1) described by Turpin *et al.* [1994] and Kirchstetter *et al.* [2001] was used to adjust estimates of TC for the positive sampling artifact that results from the adsorption of organic gases on the quartz filter substrates used to collect the particles.

2.3.3. Black Carbon (BC) Analysis

[9] BC (or soot) concentrations were estimated with an optical transmission technique, similar to that described by Rosen and Novakov [1983]. This method compares the attenuation of white light through a loaded filter relative to that of a blank filter. The relationship between optical attenuation (ATN) and the BC concentration ($\mu\text{g cm}^{-2}$) is given by $\text{ATN} = \sigma \cdot \text{BC}$, where $\text{ATN} = 100 \ln(I_0/I)$, where I_0 and I are the transmitted light intensities through the blank and loaded filters, respectively, and σ is the mass absorption cross section for BC deposited on quartz ($\text{m}^2 \text{g}^{-1}$) [Gundel *et al.*, 1984]. A value of $20 \text{ m}^2 \text{g}^{-1}$ was used for the mass absorption cross section.

2.3.4. Ion Chromatographic Analysis

[10] A Dionex Model 500 ion chromatograph with a separator column, anion fiber suppressor, and conductivity detector was used for the analysis of collected samples for nitrate and sulfate. Sample filters were ultrasonically extracted and the concentrations of sulfate and nitrate in the various solutions determined by peak area measurement and comparison to standards. Sulfate was determined by IC analysis of aqueous extracts of the Q₃ Teflon filter and a portion of the Q₄, and Q₅ quartz filters. Nitrate material retained by the Q₄ or Q₅ quartz filters (defined as “non-volatile” in this paper) and lost from particles during

sampling and collected on the C₄ or C₅ charcoal filter (defined as “semivolatile” in this paper) were determined by IC analysis of aqueous (Q₄ or Q₅) or eluent (C₄ or C₅) extracts.

3. Results

3.1. Data Precision

[11] The precision of the sulfate, nitrate and carbonaceous material results obtained from the filter packs 4 and 5 replicates are given in Table 1.

3.2. Quartz Filter Results

[12] Direct comparison of the various quartz filter results is complicated by the possible presence of several sampling artifacts. The positive artifact [Turpin *et al.*, 1994; Eatough, 1999] is the portion of TC on the front quartz filter (QF) that is the result of absorbed organic gases, rather than collected particles. This artifact is expected to be present on filter Q₂ in Figure 1. However, the positive artifact should not be present on filters T₁ or T₃ in Figure 1 because a Teflon filter is not expected to absorb gas-phase organic compounds [Turpin *et al.*, 1994]. Likewise, the positive artifact is not expected to be present on the quartz filters after the particle concentrator and the BOSS denuder, Q₄ and Q₅ in Figure 1, because the gas-phase compounds that can adsorb on a quartz filter are effectively removed in the particle concentrator–denuder combination [Ding *et al.*, 2002; Lewtas *et al.*, 2001].

[13] A second artifact that may affect the collection of particulate organic material is the loss of SVOC from the particles collected on the quartz filter during sampling [Eatough, 1999]. This negative artifact may affect collection of particles on any of the initial filters in the sampling system (e.g., T₁, Q₂, T₃, Q₄, and Q₅ in Figure 1). If the particle collecting filter is Teflon, the SVOC will pass through the Teflon filter. However, if the particle collection filter is quartz, some of the SVOC lost from the particles during sampling may be reabsorbed by the quartz filter that is collecting the particles.

[14] The data obtained for carbonaceous material present on the Q₂ filter were interpreted using the assumption of Turpin *et al.* [1994], namely, that negligible particulate SVOC which can be subsequently collected by a quartz filter is lost from the particles. Based on this assumption, three estimates of total nonvolatile particulate carbon (TC) for the Q₂ filter are given here: uncorrected TC (based on the results for the analysis of the Q₂ filter only), and two estimates of TC corrected for the positive artifact. Both the quartz-behind-quartz (Q_{2.2} filter, QBQ) and the quartz-

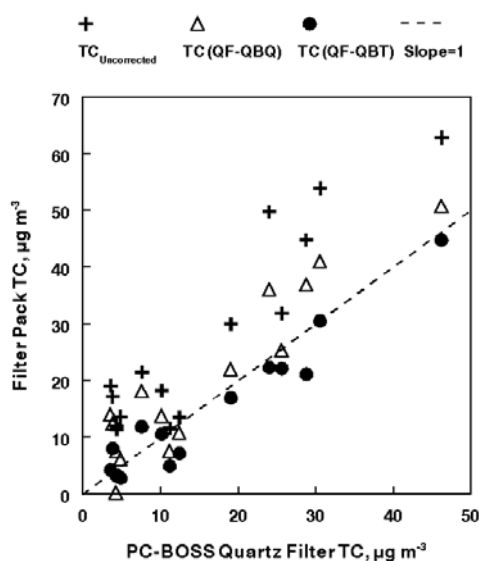


Figure 2. Comparison of TC determined on the PC-BOSS quartz filters with the $TC_{Uncorrected}$ measurement on a Q_2 filter and Q_2 filter corrected for the carbon on the $Q_{2.2}$ filter after the Q_2 filter, TC (QF-QBQ), or corrected for the carbon on the Q_1 filter after the Teflon, T_1 , filter, TC (QF-QBT) (Figure 1).

behind-Teflon (Q_1 filter, QBT) filters were used to correct for this artifact. As described by *Turpin et al.* [1994], the QBT is expected to be the preferred measure of the positive artifact. Therefore, our best estimate of Q_2 TC corrected for the positive artifact is TC (QF-QBT). As mentioned above, the Q_4 and Q_5 filters are not expected to have a positive artifact. In addition, it has generally been observed [Eatough, 1999] that the negative artifact for a quartz filter is independent of whether or not it is preceded by a denuder. The results obtained for Q_2 $TC_{Uncorrected}$, for QF-QBT and for QF-QBQ, and for the averages of Q_4 and Q_5 TC (PC-BOSS TC), are given in Figure 2. The linear regression, variance, and t test results for these comparisons are given in Table 2.

3.3. Fine Particulate Composition and Concentration

[15] Fine particulate material can be composed of a wide range of species, but in this paper particulate composition is constructed from carbonaceous material, consisting of elemental carbon (BC or soot) and organic material (assumed

to be 61% carbon) [Turpin and Lim, 2001], sulfate as ammonium sulfate, and nitrate as ammonium nitrate. The average concentrations and composition of constructed fine particulate material determined from the PC-BOSS samples for the eight flight categories defined above are shown in Figure 3. The concentrations and composition for each of the samples included in the average were comparable. To allow the comparison of data collected at various temperatures and altitudes, the data used to derive the averages in Figure 2 are all converted to 25°C and 1 atm.

4. Discussion

4.1. Data Precision

[16] The precision and accuracy of the data obtained with the PC-BOSS were evaluated by comparison of results obtained for two PC-BOSS filter packs and by comparison of results obtained with the various filters included in the sampler (Figure 1). The variance, σ , between each compared data set was calculated from (1), where $C_{1,i}$ and $C_{2,i}$ are concentrations of the chemical species of interest, and the term $(\bar{X}_1 - \bar{X}_2)$ corrects the standard deviation for bias between the two replicate data sets:

$$\sigma = \left[\frac{1}{2N} \sum (X_{i,1} - X_{i,2}) - (\bar{X}_1 - \bar{X}_2) \right]^2 \quad (1)$$

The percentage precision for the replicate sets was calculated from (2):

$$\sigma\% = \frac{\sigma}{\frac{1}{2}(\bar{X}_1 + \bar{X}_2)} \times 100 \quad (2)$$

Each data set was also compared by linear regression analysis. In these analyses, both the regression calculated intercept and a slope with a zero intercept were calculated. Finally, the various filter pack comparisons were evaluated with a two-tailed Student t test at the 90% confidence level.

[17] The results of these various statistical analyses are given in Table 1 for the replicate filter comparisons and in Table 2 for the comparisons between different types of filters. The precision for the replicate data obtained for the PC-BOSS sampler is about $\pm 0.6 \mu\text{g m}^{-3}$ for inorganic ammonium sulfate and ammonium nitrate (expressed as the salts), or $\pm 9\%$ and $\pm 19\%$ for these two species, respectively (Table 1). The precision of the organic material averaged $\pm 2.2 \mu\text{g m}^{-3}$ for either nonvolatile organic mate-

Table 2. Results of the Statistical Analysis of Total Particulate Carbon Results on the Various PC-BOSS and Filter Pack Samples^a

X versus Y	N	Linear Regression			X^b Average	$X - Y^b$ Bias	σ^b	$\sigma\%^c$	Two-tailed t test P (10%)
		R^2	Slope ^d	Intercept					
PC-BOSS Quartz TC versus Q_2 $TC_{Uncorrected}$	15	0.78	1.56 ± 0.10	0 ± 8.1	15.72	11.74	NA	NA	0.04
PC-BOSS Quartz TC versus Q_2 TC (QF-QBQ)	15	0.86	1.26 ± 0.14	7.7 ± 6.6	15.72	4.47	1.90	10.6	0.38
		0.87	1.08 ± 0.11	3.2 ± 5.5					
PC-BOSS Quartz TC versus Q_2 TC (QF-QBT)	15	0.93	0.91 ± 0.04	0 ± 3.1	15.72	-1.42	2.05	13.6	0.76
		0.93	0.91 ± 0.07	0.0 ± 3.2					

^aConcentrations are $\mu\text{g m}^{-3}$.

^bSee (1).

^cSee (2).

^dSlopes are given for (1) zero intercept and (2) calculated intercept.

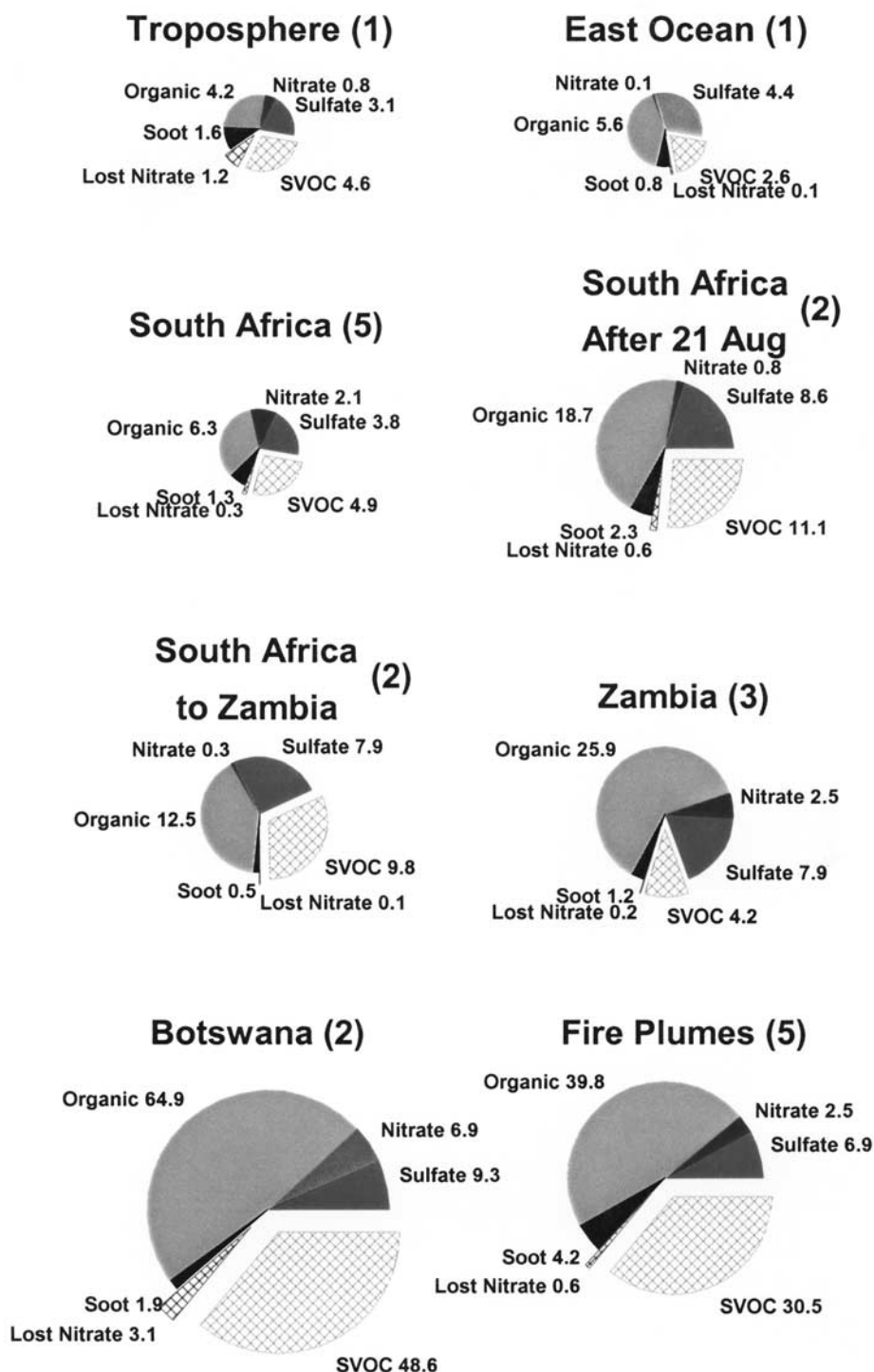


Figure 3. Average composition of fine particulate material ($\mu\text{g m}^{-3}$) collected on flights in the free troposphere (UW flight 1821), east Indian Ocean (Inhaca Island, UW flight 1822), boundary layer over South Africa before 21 August (UW flights 1819, 1812, 1814, 1815, and 1819), boundary layer over South Africa after 22 August (UW flights 1820 and 1822), boundary layer over the South Africa–Zambia Border (UW flights 1823 and 1826), boundary layer over Zambia (UW flights 1829 and 1831), boundary layer over Botswana (UW flights 1832 and 1833), and savanna fire plumes (UW flights 1816, 1819, 1826, 1834, and 1831). The area of each pie chart is proportional to the total fine particulate concentration. See color version of this figure at back of this issue.

rial or SVOC lost from particles during sampling. This value is $\pm 13\%$ of the average concentrations.

4.2. Quartz Filter Data

[18] The results for carbonaceous material collected on the various quartz filters in the sampler shown in Figure 1 are compared in Figure 2 with the statistical comparisons given in Table 2. Included are the comparisons of results obtained for the average of the PC-BOSS Q_4 and Q_5 total carbonaceous material measurements, the result obtained for carbonaceous material on filter Q_2 ($TC_{Uncorrected}$), Q_2 results corrected for the second quartz filter $Q_{2,2}$ results, TC (QF-QBQ), and Q_2 results corrected for the quartz filter after the Teflon filter Q_1 results, TC (QF-QBT). A typical example of each of these comparisons is given in Figure 4 for the sample collected in the plume of a savanna fire on 1 September 2000 (UW flight 1826). As indicated in Figure 2 and Table 2, the $TC_{Uncorrected}$ quartz filter results averaged $11 \mu\text{g C m}^{-3}$ higher than the PC-BOSS quartz filter results. The difference between these two results was mainly due to organic material that evolved from the quartz filter below 200°C (Figure 4). It would be expected that this material would be dominated by gas-phase organic compounds adsorbed by the quartz filter during sampling, because these compounds were removed by the BOSS denuder for the PC-BOSS results. Correction of the Q_2 carbon analysis for the carbon found on a second quartz filter produced TC (QF-QBQ) results that were still biased higher than the PC-BOSS quartz filter results (Figure 2 and Table 2), although they were not statistically different by the two-tailed t test. As illustrated by the comparison shown in Figure 4, the difference between these two results is still due to higher concentrations of organic material evolved below 200°C (Figure 4). However, the difference for the TC (QF-QBQ) results is much lower than for the $TC_{Uncorrected}$ results (Figure 2).

[19] Correction of the Q_2 carbon analysis for the carbon found on the quartz filter after a Teflon filter gave TC (QF-

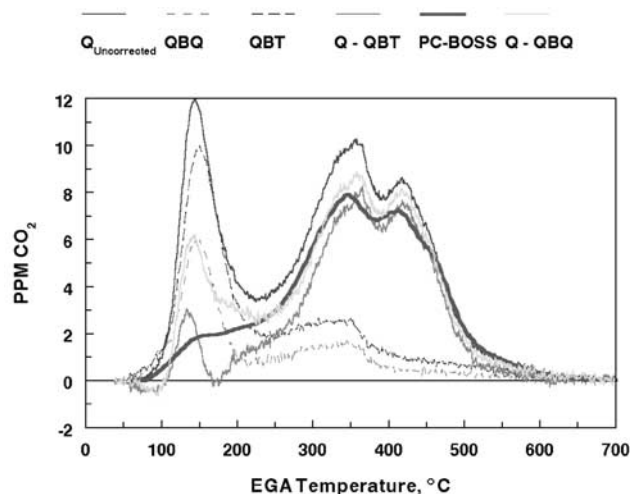


Figure 4. Thermograms for the analysis of quartz filters collected on 1 September 2000 (UW flight 1826) in the plume of a savanna fire. See color version of this figure at back of this issue.

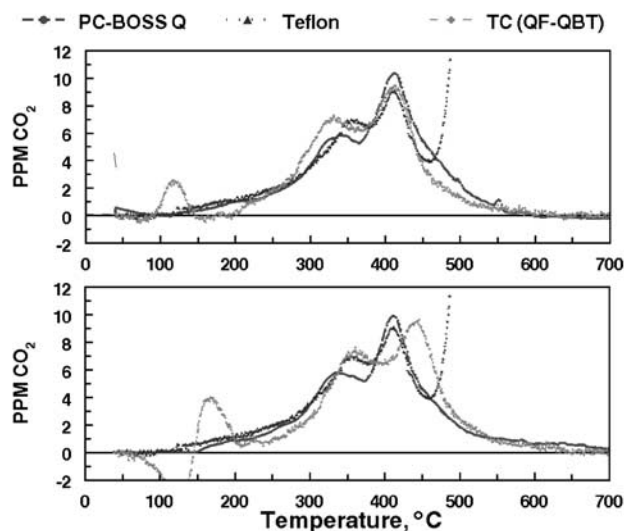


Figure 5. Thermograms for the analysis of quartz and Teflon filters collected during two sampling periods on 2 September 2000 (UW flight 1829) in the boundary layer over Zambia with influence from aged smoke from savanna fires. See color version of this figure at back of this issue.

QBT) results biased slightly lower than the PC-BOSS filter results but not statistically different (Figure 2 and Table 2). The difference between the PC-BOSS quartz filter results and the TC (QF-QBT) correction is due to lower concentrations of evolved organic material below 300°C for the TC (QF-QBT) correction. It is possible that the difference in these comparisons is due to the relative importance of SVOC lost from particles during sample collection and subsequently adsorbed by the particle collecting quartz filter [Eatough, 1999]. This material may be removed on the first quartz filter and not be collected by a second quartz filter. If the amount of gas-phase organic material collected by a second quartz filter is lower than that collected by the first quartz filter [Turpin *et al.*, 1994], the TC (QF-QBQ) correction would be higher than the PC-BOSS result, as shown in Figure 4. However, this gas-phase material would not be trapped by a Teflon filter, and the quartz filter after the Teflon filter would trap this material (which is also trapped by a first quartz filter), resulting in a TC (QF-QBT) correction that is lower than it should be. This underestimation is small according to the results shown in Figure 2, and the quartz filter after a Teflon filter correction is probably correct much of the time (Figure 2). This conclusion is supported by the comparison of PC-BOSS quartz filter results and the results of analysis of a Teflon filter for collected carbonaceous material. The Teflon filter can only be heated to about 450°C before decomposition of the Teflon begins. However, this analysis was done for two samples collected in the boundary layer over Zambia during UW flight 1829 on 2 September. The Teflon filter, PC-BOSS quartz filter and TC (QF-QBT) analyses for these two samples are compared in Figure 5. As illustrated, material present below 200°C is largely missing from both the PC-BOSS filter and the Teflon filter. Thus, the same concentrations are obtained from both analyses. This result suggests that, for this sample at least, there was little particulate SVOC lost from the particles and subsequently retained on the first

quartz filter. The result also suggests little or no gas-phase organic material is collected by the particles on the Teflon filter. However, the details in the thermogram for the TC (QF-QBT) analysis differ from those for the Teflon or PC-BOSS filter. The differences in the TC (QF-QBT) measurement compared to those for the Teflon or PC-BOSS filters must be due to the difference in the collection of gas-phase organic compounds and loss of SVOCs from an initial quartz filter and a quartz filter after a Teflon filter.

[20] Based on the Q_1 measurements, the positive artifact varied from 2.3 to 10.3 $\mu\text{g m}^{-3}$. The magnitude of the positive artifact, relative to the TC collected on a front quartz filter, varied from 39% to 85% and averaged 53% of the TC Q_1 values. As a result, fine particulate organic carbon concentrations, not corrected for the positive artifact, are about twice as large, on average, than concentrations corrected for the positive artifact. Previous studies have shown that the relative magnitude of the positive quartz filter artifact compared to quartz filter particle carbon is a function of flow rate [Turpin *et al.*, 2000; Cui *et al.*, 1998], with the absolute amount of gas-phase organic material reaching a maximum at high flow rates due to filter saturation. Filter saturation is suggested by the data in Figure 2. Thus, carbonaceous aerosol concentrations measured using only a single quartz filter (this includes all historical and many current measurements) are subject to significant and variable error.

[21] This section has emphasized the importance of the positive artifact. However, as is pointed out in the following section, the negative artifact is comparable in magnitude. Since both artifacts depend on a myriad of factors (e.g., sample flow rate, sampling time, temperature, relative humidity, particle and gas-phase concentrations and composition, etc.), the SAFARI 2000 data set can be used as an example of the magnitudes of these artifacts, but not a measure of the artifacts that might be measured elsewhere.

[22] In summary, the data outlined above indicate that two artifacts can affect the amounts of material collected on a quartz filter. One is the absorption of gas-phase organic material by the quartz filter. Attempts to correct for this artifact with a second quartz filter under corrects for this adsorption. The second effect is the loss of semivolatile organic material from the particles during sampling, with reabsorption of some of this material by the quartz filter collecting the particles. Correction for the gas-phase adsorption with a quartz filter after a Teflon filter does not account for any semivolatile particulate organic material lost from particles and reabsorbed by the quartz filter, and it may overcorrect the quartz filter data. However, based on the results reported here, this effect appears to be usually small.

4.3. Fine Particle Composition

[23] The average composition of fine particulate material determined from the PC-BOSS results for the eight flight categories given in section 2.2 are shown in Figure 3. The number of samples included in each category is indicated for each pie chart. Sulfate was determined from the ion chromatographic analysis of the Q_4 and Q_5 filters and is given as ammonium sulfate. Nitrate is expressed as ammonium nitrate retained by these quartz filters. Soot is the elemental or black carbon found on these same quartz filters. Organic material is the carbonaceous component retained on the quartz filters, assuming the material is 61% C [Turpin and Lim, 2001]. The

lost nitrate and the SVOC were determined from analysis of the CIG filters after the quartz filters of the PC-BOSS (Figure 1). They are expressed as ammonium nitrate and organic material (which is 61% carbon).

[24] As shown in Figure 3, substantial variations in both the chemical composition and concentrations of the fine particles were associated with the eight categories of samples. The area of the various graphs in Figure 3 is proportional to the total fine particulate concentration. The lowest concentrations were obtained in the UW flight 1821 in the free troposphere, and UW flight 1822 above Inhaca Island, Mozambique, in the East Ocean. Similar concentrations and compositions were obtained for these two samples, but with slightly more SVOC and less nonvolatile organic material in the free troposphere sample. The concentration and composition of fine particulate material in the boundary layer over South Africa prior to 21 August was comparable to that found in the free troposphere. During these flights (UW 1810, 1812, 1814, 1815, and 1819) [Hobbs, 2001; Sinha *et al.*, 2003] over central South Africa, the low organic material concentrations indicate that the region may have been little affected by emissions from savanna fires. However, an increase in fine particulate material, but with similar composition, was seen in two samples collected in the boundary layer over South Africa shortly after 21 August (UW flights 1820 and 1822 on 22 and 24 September, respectively). The samples in the boundary layer over Zambia and Botswana were collected after all of the South Africa samples. A marked increase in fine particulate material concentration was seen in going from South Africa to Zambia to Botswana. This is the direction of the counterclockwise gyre over the subcontinent. Thus, the increase in the fine particulate mass in the more northerly samples may reflect the increased importance of aged emissions from increasing numbers of savanna fires. During the time period when the Botswana samples were collected (UW flights 1832 and 1833, 6 September) there was a large decrease in visibility over the region flown by the Convair-580, compared to flights over Zambia on 3 and 5 September. This was due to the transport of thick, aged smoke from the north (H. Annegarn *et al.*, "The River of Smoke": Characteristics of the southern African springtime biomass burning haze, submitted to *Journal of Geophysical Research*, 2003). A marked increase in the organic fraction (both nonvolatile and SVOC) accompanied the increase in aged fine particles from savanna fire emissions. The samples collected over Botswana were similar in composition to the particles collected during passage through smoke plumes. However, the concentrations seen in the boundary layer over Botswana were higher than that seen in repeated passage through isolated plumes. The lower average concentrations obtained in the plume samples reflects the lower background concentrations associated with the plume sample collection and the relatively short plume residence time compared to the entire sampling period. The plume and Botswana samples were dominated by organic material, and SVOC averaged 24% and 36%, respectively, of the fine particulate material in these samples.

5. Conclusions

[25] Comparison of PC-BOSS and Q/Q and T/Q filter pack data collected in SAFARI 2000 indicate that both

positive and negative carbonaceous material artifacts were important. The positive artifact is best corrected for in filter pack samplers using a quartz filter behind a Teflon filter. Likewise, the PC-BOSS sampler eliminates the positive artifact because of the particle concentrator/denuder combination in this sampler. However, only the PC-BOSS with the charcoal impregnated sorbent filter after a quartz filter can correct for the negative artifact due to the loss of SVOC from particles during sampling.

[26] Fine particles in fresh emissions from savanna fires were dominated by carbonaceous material. These particles averaged 5% elemental carbon, 47% nonvolatile organic material and 35% SVOC. Concentrations of fine particles in the atmospheric boundary layer averaged $19 \mu\text{g m}^{-3}$ when there was relatively little impact from aged savanna fire emissions, and $135 \mu\text{g m}^{-3}$ with substantial impact from aged savanna fire emissions. The aged smoke averaged 2% elemental carbon, 48% nonvolatile organic material, and 36% SVOC. In addition, the aged aerosol mass averaged 5% nitrate retained by the particles during sampling and 2% nitrate lost from the particles during sampling. Thus, semi-volatile materials, which could not be measured by conventional filter samplers, averaged 38% of the total fine particulate mass in aged aerosols from savanna fires. This material could have a significant impact on the climate of the region.

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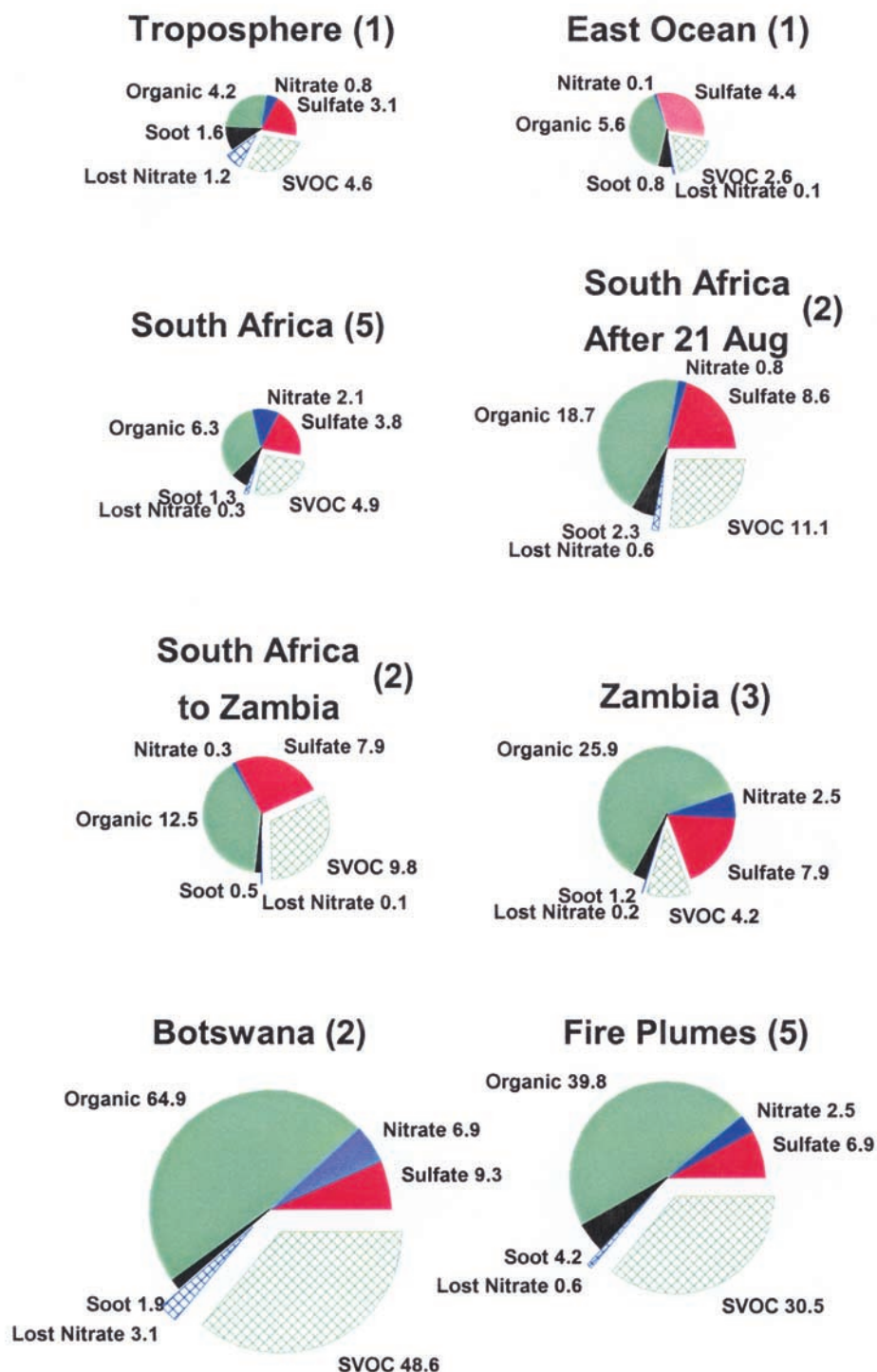


Figure 3. Average composition of fine particulate material ($\mu\text{g m}^{-3}$) collected on flights in the free troposphere (UW flight 1821), east Indian Ocean (Inhaca Island, UW flight 1822), boundary layer over South Africa before 21 August (UW flights 1819, 1812, 1814, 1815, and 1819), boundary layer over South Africa after 22 August (UW flights 1820 and 1822), boundary layer over the South Africa–Zambia Border (UW flights 1823 and 1826), boundary layer over Zambia (UW flights 1829 and 1831), boundary layer over Botswana (UW flights 1832 and 1833), and savanna fire plumes (UW flights 1816, 1819, 1826, 1834, and 1831). The area of each pie chart is proportional to the total fine particulate concentration.

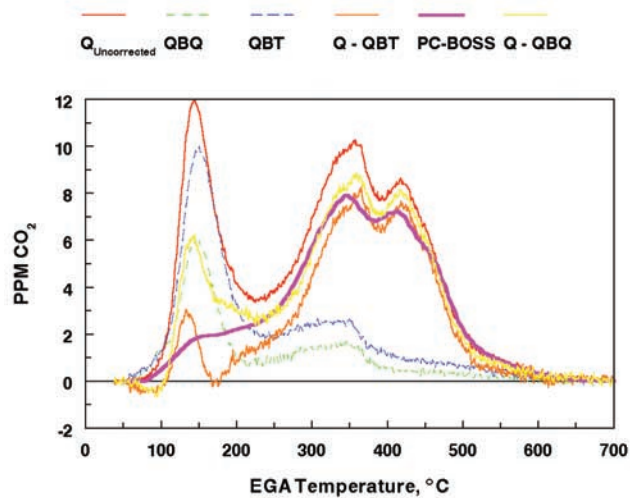


Figure 4. Thermograms for the analysis of quartz filters collected on 1 September 2000 (UW flight 1826) in the plume of a savanna fire.

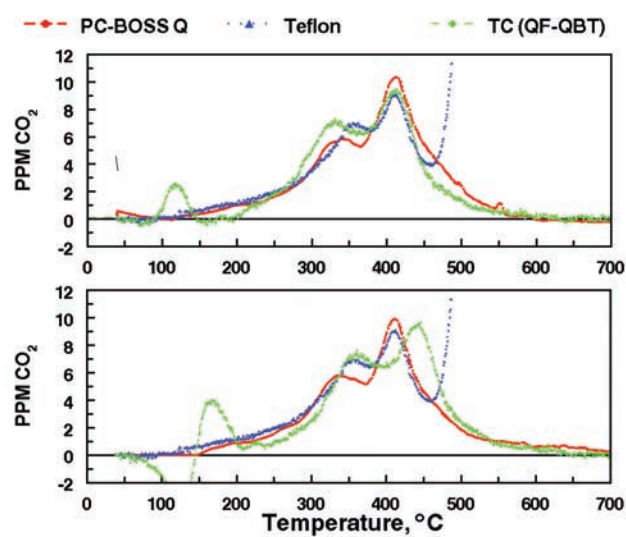


Figure 5. Thermograms for the analysis of quartz and Teflon filters collected during two sampling periods on 2 September 2000 (UW flight 1829) in the boundary layer over Zambia with influence from aged smoke from savanna fires.